



Publicationsnummer: **0 551 749 A2**

EUROPEAN PATENT APPLICATION

(21) Application number: **92311555.4**

(51) Int. Cl.⁶: **A61K 7/06**

(22) Date of filing: **17.12.92**

(30) Priority: **20.12.91 US 812529**

(43) Date of publication of application:
21.07.93 Bulletin 93/29

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE

(71) Applicant: **UNILEVER PLC**
Unilever House Blackfriars
London EC4P 4BQ (GB)

(84) **GB IE**

(71) Applicant: **UNILEVER N.V.**
Weena 455
NL-3013 AL Rotterdam (NL)

(84) **BE CH DE DK ES FR GR IT LI NL PT SE AT**

(72) Inventor: **Lee, Jae G.**
36 Stonehouse Road, Trumbull
Fairfield, Connecticut 06611 (US)
Inventor: **Vinski, Paul**
202 Mamasco Road No. 17, Ridgefield
Fairfield, Connecticut 06877 (US)

(74) Representative: **Bristow, Stephen Robert et al**
Unilever PLC Patent Division Colworth House
Sharnbrook
Bedford MK44 1LQ (GB)

(54) **Hair treatment composition.**

(57) A hair treatment composition is provided that includes a water-insoluble, dispersible polymeric resin having a viscosity of less than 2 centipoise at 25°C when dispersed at 10% in water and a water-soluble amphoteric polymer.

has amphomer and
AQ 55 } presumably linear?
T_g is much higher
than AQ 1350.
(branched)

EP 0 551 749 A2

BACKGROUND OF THE INVENTIONField of the Invention

5 The invention relates to hairspray compositions especially formulated for use in low organic volatile systems.

Related Art

10 Hairspray compositions must meet a number of functional requirements. These include good holding ability and curl retention without giving a harsh, brittle feeling to the hair. Even under humid conditions there must be good hold and curl retention. Another requirement is that the hairspray be capable of being removed upon washing the hair at the time of shampooing. Additionally, the compositions must include the properties of low stickiness, good combing characteristics and a lack of powdering or flaking.

15 Various resins have been employed in hairspray compositions to achieve the aforementioned desirable properties. Among such resins are the amphoteric and anionic types.

Amphoteric resins have been extensively employed. These polymers contain cationic radicals derived from monomers such as t-butyl aminoethyl methacrylate as well as carboxyl radicals derived from monomers such as acrylic acid or methacrylic acid. Representative of this group is a product manufactured by the National Starch and Chemical Corp. under the trademark Amphomer identified on product labels by the CTFA name of Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymers. Use of Amphomer alone or in conjunction with other resins for hairsprays has been reported in U.S. 3,927,199 (Micchelli et al), U.S. 4,402,977 (Grol-
 20 lier et al), U.S. 4,859,455 (Nowak, Jr. et al), U.S. 4,871,529 (Sramek), U.S. 4,983,383 (Maksimoski et al), U.S. 4,983,418 (Murphy et al), U.S. 5,021,238 (Martino et al), GB 2,098,624 (Madrang) and Canadian Patent 1,222,461 (Varco).

25 Anionic polymeric resins have also been utilized in this art. For instance, U.S. 4,300,580 (O'Neill et al) discloses linear polyesters prepared from isophthalic acid, the sodium salt of 5-sulphoisophthalic acid and diethylene glycol. Eastman AQ Polymers for water-dispersed hairsprays are based on this technology. Other polyester and sulpho substituted polymer systems are described in U.S. 4,525,524 (Tung et al).

30 Environmental concerns and legislation addressing such concerns have required product reformulations to meet these challenges. Organic solvent-based sprays must, at least in part, now be substituted by water systems. Levels of organic propellants present in these water systems must also be adjusted to relatively low levels. With these constraints, certain problems have arisen. Water-dispersed systems are slow to dry. Not only do they result in wet hair but there is also an undesirable chill sensation. Quite significantly there is also
 35 difficulty in styling the hair. Resins formulated in a water-dispersed system have weak holding power.

Some systems such as the Eastman AQ Resins have good setting or holding but removability from hair is quite poor because these resins are not water soluble.

40 Furthermore, there is the problem of difficulties in pumpability of certain types of resins such as some amphoteric. A still further problem is that of improving glossiness to counteract resins that usually tend to dull hair.

Accordingly, it is an object of the present invention to provide a hairspray suitable for water-dispersed systems having improved holding and styling characteristics.

Another object of the present invention is to provide a hairspray composition based on a water-dispersed system that dries fairly quickly and does not impart a wet or cool feel to hair or scalp.

45 A further object of the present invention is to provide a hairspray composition for water-dispersed systems that improves glossiness of the hair.

A still further object of the present invention is to provide a hairspray composition for water-dispersed systems being sufficiently nonviscous for easy pumpability and to exhibit a viscosity between 3 and 7.5 centipoise at 25°C.

50 These and other objects of the present invention will become more evident from the following summary and detailed description.

SUMMARY OF THE INVENTION

55 A hair treatment composition is provided comprising:

- (i) a water-insoluble, dispersible polymeric resin having a viscosity of less than about 2 centipoise at 25°C when 10% is dispersed in water, present in an effective amount for setting hair; and
- (ii) a water-soluble amphoteric polymer present in an effective amount for setting hair.

Fixing

facky?

Hair treatment compositions of this invention are dispersed in water and are especially suited for delivery through nonpressurized mechanical pumps.

DETAILED DESCRIPTION

5

Now it has been discovered that many of the objects of the present invention can be achieved by using a hair treatment composition that includes a water-insoluble, dispersible polymeric resin having a viscosity of less than 2 centipoise at 25°C (when dispersed at 10% in water) and a water-soluble amphoteric polymer. Each of these two components interact with the other to provide an overall superior hairspray. The water-insoluble resin provides a good to moderate hold while importantly maintaining a low viscosity, i.e. not higher than 3.0 centipoise at 25°C. On the other hand, the water-soluble amphoteric polymer provides a very substantial hold but the concentration thereof must be limited to avoid excessive thickness, i.e. above 7.5 centipoise at 25°C. The amphoteric polymer is also quite important for aiding in removing the water-insoluble resin from the hair upon shampooing.

A variety of water-insoluble dispersible polymeric resins may be employed for this invention. Most preferred are polyesters functionalized with a sulpho (SO_3^-) group in amounts sufficient to water-disperse the polyester. Illustrative of such resins are Eastman AQ Polymers, especially those having a glass transition temperature ranging from about 50°C to about 70°C, preferably around 55°C. Most preferred is Eastman AQ 55S which is a polyester identified as an ethylene diglycol/cyclohexanedimethanol/isophthalates/ sulphisophthalates resin. These polyesters can be derived through esterification of:

- (a) at least one dicarboxylic acid;
- (b) at least one diol, at least 20 mole percent of this diol component being a poly (ethylene glycol) having a formula $\text{H}-(\text{-OCH}_2\text{CH}_2)_n\text{OH}$ wherein n is an integer from 2 to about 10, and
- (c) at least one difunctional monomer containing a SO_3M group attached to an aromatic nucleus, wherein M is hydrogen or a metal ion such as sodium, lithium or potassium.

Preferably the sulpho-monomer component constitutes at least from about 8 to 45 mole percent of the sum of the moles of components (a) and (c), the acid components and the diol being substantially equimolar.

Amounts of the water-insoluble dispersible polymeric resin will range from about 0.5 to about 10%, preferably from about 1.5 to about 8%, optimally between about 2 and about 6% by weight.

The second component of the present invention is a water-soluble amphoteric polymer. Advantageously, this polymer is an acrylate copolymer, especially an octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer. Such material is available from the National Starch and Chemical Company under the trademark AMPHOMER LV-71. The acrylate-based copolymers are generally defined as containing from 40 to 60% of a $\text{C}_3\text{-C}_{12}$, preferably $\text{C}_3\text{-C}_8$, alkyl methacrylate, 20 to 40% of a $\text{C}_4\text{-C}_{10}$ N-substituted alkyl acrylamide, and 10 to 25%, preferably 19 to 25% acrylic acid or methacrylic acid, wherein the percentages total 100%. More preferably, these copolymers comprise 45-55% isobutylmethacrylate, 25 to 35% N-t-octyl acrylamide, and 19 to 25% acrylic acid.

Amounts of the water-soluble amphoteric polymer resin may range from about 0.5 to about 10%, preferably from about 1.5 to about 5%, optimally between about 2 and about 4% by weight.

Compositions of the present invention will also include water as a solvent carrier for the resins and other components. Water will be present in amounts ranging from about 10% to about 99%, preferably from about 40% to about 95% by weight.

With certain of the resins it may be necessary to neutralize some acidic groups to promote solubility/dispersibility. Examples of suitable neutralizing agents include 2-amino-2-methyl-1,3-propanediol (AMPD); 2-amino-2-ethyl-1,3-propanediol (AEPD); 2-amino-2-methyl-1-propanol (AMP); 2-amino-1-butanol (AB); monoethanolamine (MEA); diethanolamine (DEA); triethanolamine (TEA); monoisopropanolamine (MIPA); diisopropanol-amine (DIPA); triisopropanolamine (TIPA); and dimethyl stearamine (DMS). Amounts of the neutralizing agents will range from about 0.001 to about 10% by weight.

The present hairspray compositions may be formulated in aerosol or nonaerosol forms. However, the compositions are particularly useful in nonaerosol form to be delivered by a mechanical pump spray.

Small quantities of surfactant ranging anywhere from 0.1 to about 10%, preferably from about 0.1 to about 1%, optimally about 0.3% by weight may be present in the compositions of the invention. The surfactant may be an anionic, nonionic or cationic emulsifier. Particularly preferred are nonionic emulsifiers which are formed from alkoxylated hydrophobes such as fatty alcohols, fatty acids and phenols. Illustrative of such material is Triton X-100, and isooctyl phenyl polyethoxy-ethanol.

Resins when deposited upon hair quite often impart dullness. Counteraction of the dullness effect may be achieved by incorporating low levels of $\text{C}_{10}\text{-C}_{20}$ fatty alcohol esters. Particularly preferred is cetyl octanoate. Amounts of these lustrating agents will range from about 0.001 to about 1%, preferably from about 0.01

to about 0.5%, optimally from about 0.02 to about 0.1% by weight.

Compositions of this invention may contain any other ingredient normally used in hairsprays. These other ingredients may include antifoam agents, preservatives, antioxidants, fragrances, antimicrobials and sunscreens. Each of these ingredients will be present in an amount sufficient to accomplish its purpose.

The following examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein and the appended claims are by weight unless otherwise indicated.

EXAMPLE 1

Hairspray composition typical of the present invention is outlined below.

Component	Weight Percent
Water	92.975
Amphomer LV-71	3.300
Eastman AQ 55	2.200
AMP-95	0.693
Triton X-100	0.300
Methylparaben	0.200
Fragrance	0.150
Dow Corning 190 SU	0.100
DMDM Hydantoin	0.050
DL-panthenol	0.001
Vitamin E Acetate	0.001

EXAMPLE 2

A series of experiments were conducted to evaluate the most effective relative concentrations of the Eastman AQ 55S resin to the Amphomer LV-71 polymer. These experiments utilized the following test procedure.

Film "hardness", a measure of hair hold capability, was evaluated by evenly applying 2-4 grams of concentrate onto a 20 cm x 20 cm glass plate. Samples were allowed to dry overnight to achieve a thick, dry film. Observations of gelling of the film were recorded. Using a sharp-pointed tool, the film was lightly "scratched" upon the glass plate. Observations were then recorded with regard to hardness and brittleness. A ranking was performed in comparison with known controls.

The above test was performed on the composition of Example 1 except for the stated variations in resin and polymer. Table 1 outlines spray characteristics and hair hold capability as a function of resin to polymer ratios.

TABLE 1

Composition	Ratio of AQ 55S:Amphomer	Spray Characteristics	Hair Hold Capability
I-A	100:0	Too misty; Uncontrollable	poor hold
I-B	80:20	Acceptable	Acceptable
I-C	60:40	Acceptable	Acceptable
I-D	40:60	Acceptable	Acceptable
I-E	20:80	Acceptable	Acceptable
I-F	0:100	Too coarse to spray; clogs valve and spits	Better hold

Composition I-D having a ratio of AQ resin to Amphomer of 40:60 exhibited the optimum performance in spray characteristics and hair hold capability. The acceptable range for spray characteristics was from 80:20 to 20:80 ratio of the respective resin and polymer.

The foregoing description and Examples illustrate selected embodiments of the present invention. In light thereof, various modifications will be suggested to one skilled in the art, all of which are within the spirit and purview of this invention.

Comparative Test 1

A series of formulations as taught in US 440 2977 (A-F) were compared with a formulation according to the present invention. The Formulas A-G were prepared using AMPHOMER and water-soluble anionic polymers listed in US 440 2977 under Table II and column 15 (lines 2-5).

Formulation	Composition	Weight %
A	Amphomer	3.30
	Resin 28-29-30	2.20
	AMP to pH 6.5-7.0	
	Deionized Water	QS to 100
B	Amphomer	3.30
	Resin 28-29-30	2.20
	AMP to pH 6.5-7.0	
	Octoxynol-9	10.00
C	Deionized Water	QS to 100
	Amphomer	3.30
	Darvan 7	2.20
	(sodium polymethacrylate)	
	NaOH (1N) to pH 7.5-8.0	
	Deionized Water	QS to 100

5	D	Amphomer	3.30
		Darvan 7	2.20
		(sodium polymethacrylate)	
		TEA Lauryl Sulfate	8.50
		NaOH (1N) to pH 7.5-8.0	
10	E	Deionized Water	QS to 100
		Amphomer	3.30
		Flexan 130	2.20
		(sodium polystyrene sulphonate)	
		NaOH (1N) to pH 8.00	
15	F	Deionized Water	QS to 100
		Amphomer	3.30
		Flexan 130	2.20
		(sodium polystyrene sulphonate)	
		TEA Lauryl Sulfate	8.50
20	G	Deionized Water	QS to 100
		Amphomer	3.30
		AQ 55S	2.20
		AMP	0.69
		Deionized Water	QS to 100

35 Hair hold capability was measured in accordance with the procedure of Example II and the results are given in Table II below:

TABLE II

40	Hair Hold Capability Evaluation	
	Formula	Holding Power
45	A	Poor
	B	Very Poor
50	C	Poor
	D	Poor
55	E	Poor - Good
	F	Poor
	G	Good - Very Good

From Table II it is evident that combinations (Formula A-G) of the ampholytic polymer with that of various anionic polymers listed in US 440 2977 do not achieve the same good hair hold properties as those of the present invention (Formula G). Even the presence of sulphonate groups such as in Flexan 130 do not provide

adequate hair hold.

Comparative Test 2

- 5 The following experiments were performed to distinguish the present invention over US 499 6252. Formulas H-I were prepared to evaluate combinations of Eastmand AQ 55S with Joncryl polyacrylate resins. These formulas were compared with that of Formula G illustrative of the presently claimed invention.

Formula	Components	Weight %
H	AQ 55S	2.20
	Joncryl 77	3.30
	HCl (1N) to pH 7.0-7.5	
	Deionized Water	QS to 100
I	AQ 55S	2.20
	Joncryl 134	3.30
	HCL (1N) to pH 7.0-7.5	
	Deionized Water	QS to 100
G	Amphomer	3.30
	AQ 55S	2.20
	AMP	0.69
	Deionized Water	QS to 100

Hair hold capability was measured in accordance with the procedure of Example II above. The results are recorded in Table III below:

TABLE III

Hair Hold Capability Evaluation	
Formula	Holding Power
A	Poor
B	Poor
C	Good - Very Good

- 45 From Table III it is evident that to get good hold an amphoteric polymer is necessary in combination with a water-soluble substance such as Eastman AQ 55S.

Claims

- 50 1. A hair treatment composition comprising:
- (i) a water-insoluble, dispersible polymeric resin having a viscosity of less than about 2 centipoise at 25°C when 10% is dispersed in water, present in an effective amount for setting hair; and
 - (ii) a water-soluble amphoteric polymer present in an effective amount for setting hair, wherein said water-insoluble resin and amphoteric polymer have a relative ratio of 80:20 to 20:80 by weight.
- 55 2. A composition according to claim 1 wherein said water-insoluble, dispersible polymeric resin is a polymer formed from a combination of at least one dicarboxylic acid, at least one diol, and at least one difunctional

monomer containing a sulpho group on an aromatic nucleus.

3. A composition according to claim 2 wherein said water-insoluble, dispersible polymeric resin is a diglycol/cyclohexanediol/methanol/isophthalates/sulphoisophthalates polyester.
- 5 4. A composition according to claim 1 wherein said water-soluble amphoteric polymer is an acrylate copolymer.
- 10 5. A composition according to claim 4 wherein said acrylate copolymer is an acrylamide/acrylate/butylaminoethyl methacrylate copolymer.
6. A composition according to claim 1 further comprising a C₁₀-C₂₀ fatty acid ester present in an effective amount to provide lustre to hair.
- 15 7. A composition according to claim 6 wherein said ester is cetearyl octanoate present in an amount from about 0.001 to about 0.5% by weight.
8. A composition according to claim 1 wherein water is present in an amount from about 10 to about 99% by weight.

20

25

30

35

40

45

50

55